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(Acetato-κO)bis(morpholine-κN)[salicylaldehyde (2-nitrophenoxyacetyl)hydrazonato-$\kappa^3 O,N,O'$]-cobalt(III)

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The Co^{III} atom in the title complex, [Co($C_2H_3O_2$)(C_4H_9NO)$_2$($C_{15}H_{11}N_3O_5$)], is coordinated by phenol O, carbonyl O and hydrazine N atoms of the *N*-salicylaldehyde-*N*′-(*o*-nitrophenoxyacyl)hydrazone ligand, L^{2-}, one acetoxy O atom, and two N atoms of two coordinated morpholine molecules, forming an elongated octahedron. There is an intermolecular N—H···O hydrogen bond between two morpholine molecules from two neighbouring complex molecules, generating an extended chain structure.

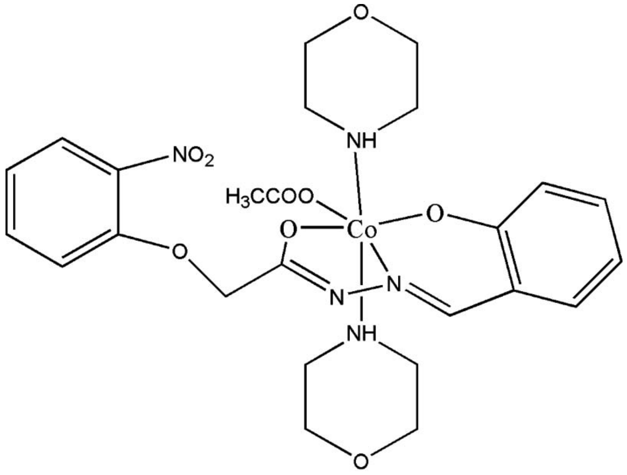
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.038
wR factor = 0.102
Data-to-parameter ratio = 17.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Recently, much attention has been focused on hydrazones and their complexes, due to their biological activities, chemical and industrial versatility, and excellent chelating capability (Liu & Gao, 1998; Iskander *et al.*, 2001; Cariati *et al.*, 2002). For example, various hydrazone compounds derived from phenoxyacetic acid are very useful for their antituberculous, antifungal, insecticidal and herbicidal activities (Lokanath *et al.*, 1998). However, to the best of our knowledge, the ligand *N*-salicylaldehyde-*N*′-(*o*-nitrophenoxyacyl)hydrazone, H_2L, and its complexes have not been reported to date. Here, we present the crystal structure of the title cobalt complex, (I), of *N*-salicylaldehyde-*N*′-(*o*-nitrophenoxyacyl)hydrazone.



(I)

As shown in Fig. 1, the Co^{III} ion in (I) is octahedrally coordinated by phenol atom O1, carbonyl atom O2 and hydrazine atom N1 from the ligand L^{2-}, one acetoxy atom (O8) and two N atoms from two morpholine molecules. Atoms O1, O2, N1 and O8 comprise the equatorial plane and the two N atoms of the morpholine molecules occupy the two axial positions.

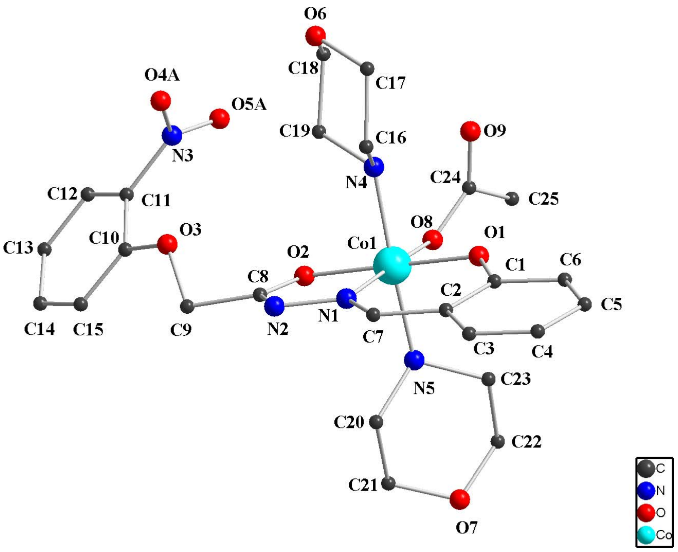


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Only a single disordered component is shown.

The Cu—O and Cu—N bond lengths (Table 1) of (I) are in agreement with those found in analogous cobalt complexes (Mondal *et al.*, 2000; Sasaki *et al.*, 1999; Amirnasr *et al.*, 2002). The Co1—N1 bond is shorter than Co1—N4 and Co1—N5, indicating that the coordination ability of diazine N is more pronounced than that of morpholine N. The difference in bond lengths can be attributed to the presence of π-back bonding in the semicarbazone moiety.

The dihedral angle between the two phenyl rings in some *N*-substituted salicylic Schiff ligands without a phenoxycarbonyl group is close to 0° (Wu & Liu, 2004). However, the dihedral angle between the two benzene rings in the phenoxyacylhydrazone ligand L^{2-} of the title complex is 44.1 (1)°. The corresponding angle in another phenoxyacylhydrazone ligand of the complex $[Ni(C_{15}H_{12}N_2O_3)(C_5H_5N)_3]$ (Chen & Liu, 2004) is 88.1°. The steric effect of the *o*-nitrate is one of the reasons for a large difference between the two dihedral angles in the two complexes with a phenoxyacyl group.

The hydrogen bonds are listed in Table 2. The N—H···O intermolecular hydrogen bond generates an extended chain structure in the complex (Fig. 2).

The successful synthesis of the title compound indicates that the Co^{II} ion undergoes an oxidation reaction in air. According to the literature (Chiari *et al.*, 2001), it is accepted that the apparent role of the extra ligand in the Co^{II} to Co^{III} oxidation process is to stabilize the latter ion by satisfying its preference for six-coordination.

Experimental

All reagents were of AR grade, available commercially and used without further purification. The ligand was prepared by condensing equimolar quantities of salicylaldehyde and *o*-nitrophenoxyacetylhydrazine in ethanol. The yellow product obtained on cooling was recrystallized from methanol. The title complex was obtained by dissolving H_2L (0.1 mmol) and $[Co(OAc)_2]\cdot 4H_2O$ (0.1 mmol) in methanol (15 ml) and adding 2 drops of morpholine. The mixture was stirred for 3 h. Red crystals of (I) were obtained from the reaction mixture on allowing it to stand overnight.

Crystal data

$[Co(C_2H_3O_2)(C_4H_9NO)_2(C_{15}H_{11}N_3O_5)]$
$M_r = 605.49$
Monoclinic, $C2/c$
$a = 27.561$ (2) Å
$b = 13.3497$ (10) Å
$c = 16.3934$ (8) Å
$\beta = 113.349$ (3)°
$V = 5537.7$ (6) Å^3
$Z = 8$

$D_x = 1.452$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6294 reflections
$\theta = 2.3$–27.2°
$\mu = 0.68$ mm^{-1}
$T = 293$ (2) K
Block, red
0.20 × 0.12 × 0.10 mm

Data collection

Rigaku Weissenberg IP diffractometer
φ scans
Absorption correction: ψ scan (*TEXRAY*; Molecular Structure Corporation, 1999)
$T_{min} = 0.752$, $T_{max} = 0.934$

6294 measured reflections
6294 independent reflections
4612 reflections with $I > 2\sigma(I)$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 35$
$k = 0 \rightarrow 17$
$l = -21 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.102$
$S = 1.02$
6294 reflections
362 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 1.6508P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

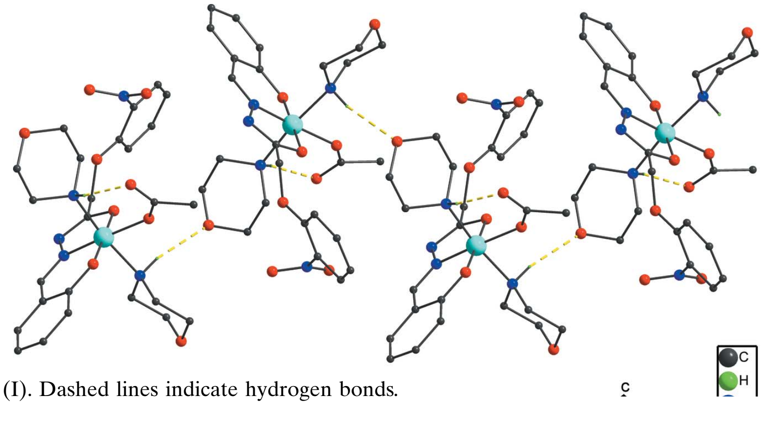


Figure 2
The extended chain structure of (I). Dashed lines indicate hydrogen bonds.

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Table 1
Selected geometric parameters (Å, °).

Co1—N1	1.8560 (17)	O7—C21	1.414 (3)
Co1—O1	1.8731 (14)	O7—C22	1.419 (3)
Co1—O2	1.8905 (13)	O1—C1	1.314 (3)
Co1—O8	1.9199 (14)	O2—C8	1.289 (2)
Co1—N4	1.9929 (17)	O3—C10	1.347 (3)
Co1—N5	2.0049 (17)	O3—C9	1.438 (2)
N1—C7	1.288 (3)	N4—C19	1.479 (3)
N1—N2	1.408 (2)	N4—C16	1.480 (3)
N2—C8	1.306 (3)	N5—C23	1.481 (3)
N3—C11	1.465 (3)	N5—C20	1.486 (3)
O6—C17	1.414 (3)	O8—C24	1.268 (2)
O6—C18	1.424 (3)	O9—C24	1.237 (3)
N1—Co1—O1	95.72 (7)	C23—N5—C20	107.60 (17)
N1—Co1—O2	83.13 (7)	C23—N5—Co1	116.86 (14)
O1—Co1—O2	178.85 (6)	C20—N5—Co1	120.55 (15)
N1—Co1—O8	172.51 (7)	C24—O8—Co1	130.95 (15)
O1—Co1—O8	90.20 (6)	O1—C1—C6	117.8 (2)
O2—Co1—O8	90.94 (6)	O1—C1—C2	124.88 (19)
N1—Co1—N4	92.73 (7)	N1—C7—C2	123.9 (2)
O1—Co1—N4	87.69 (7)	O2—C8—N2	124.89 (18)
O2—Co1—N4	92.44 (6)	O2—C8—C9	116.57 (18)
O8—Co1—N4	92.09 (7)	N2—C8—C9	118.50 (18)
N1—Co1—N5	94.40 (8)	O3—C9—C8	106.11 (16)
O1—Co1—N5	93.46 (7)	O3—C10—C11	116.3 (2)
O2—Co1—N5	86.56 (7)	O3—C10—C15	125.5 (2)
O8—Co1—N5	80.64 (7)	C12—C11—N3	118.7 (3)
N4—Co1—N5	172.63 (7)	C10—C11—N3	119.2 (2)
C7—N1—N2	118.25 (17)	N4—C16—C17	111.12 (19)
C7—N1—Co1	127.19 (15)	O6—C17—C16	112.3 (2)
N2—N1—Co1	114.57 (12)	O6—C18—C19	111.5 (2)
C8—N2—N1	107.58 (16)	N4—C19—C18	110.08 (19)
C17—O6—C18	110.15 (19)	N5—C20—C21	110.4 (2)
C21—O7—C22	110.54 (19)	O7—C21—C20	111.3 (2)
C1—O1—Co1	124.62 (14)	O7—C22—C23	111.8 (2)
C8—O2—Co1	109.36 (12)	N5—C23—C22	110.6 (2)
C10—O3—C9	118.94 (17)	O9—C24—O8	126.0 (2)
C19—N4—C16	108.10 (17)	O9—C24—C25	120.0 (2)
C19—N4—Co1	116.20 (13)	O8—C24—C25	113.9 (2)
C16—N4—Co1	119.95 (13)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H04···O9	0.92	1.96	2.753 (2)	143
N5—H05···O6^{i}	0.91	2.44	3.324 (3)	165

Symmetry code: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

Atoms O4 and O5 in the nitro group are disordered over two positions and the four split atoms were designated with the suffix *A* or *B* in the atom label. The final occupancy factors for the disordered atoms O4*A*, O4*B*, O5*A* and O5*B* are 0.60, 0.40, 0.60 and 0.40, respectively. Atoms H04 and H05 were located in a difference Fourier maps, but then allowed to ride on N4 and N5, with N—H = 0.91 and 0.92 Å. The other H atoms were positioned geometrically and constrained to ride on their attached atoms, with C—H = 0.93–0.97 Å and with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$.

Data collection: *TEXRAY* (Molecular Structure Corporation, 1999); cell refinement: *TEXRAY*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: *SHELXL97*-2 (Sheldrick,1997).

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